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Pyromellitic dianhydride is a difficult to make but a well known starting material for synthesizing polyimide polymers with excellent heat and oxidative stability. A related monomer which might be equally as good is p-benzoquinone dianhydride (1). Several attempts at making (1) resulted in low yields of the desired monomer. (orig)

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HEAT AND HYDROLYTICALLY STABLE POLYMERS FOR FABRICABLE FILMS  
AND LAMINATES

C. S. Marvel  
H. K. Hall, Jr.

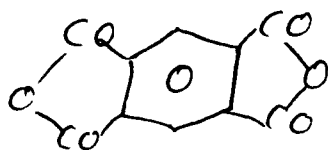
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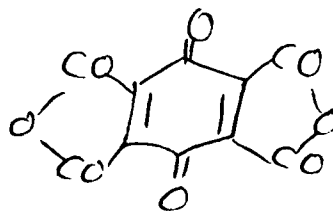
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## Results

Pyromellitic dianhydride 1 is a well-known component of polymers with excellent heat and oxidative stability such as Kapton<sup>R</sup>. p-Benzoquinone dianhydride 2 might be equally good. Brief literature reports already describe its roundabout synthesis (1) and its incorporation into polyimides (2). We have tried to devise a synthesis route which would make this interesting monomer readily available.

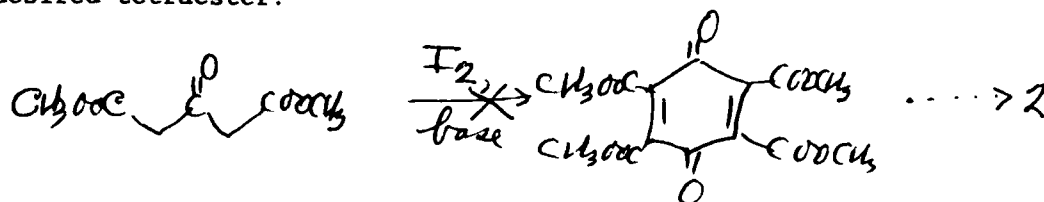


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Various attempts to improve the base-induced coupling of acetonedicarboxylic ester by iodine (1,3) failed to give more than traces of the desired tetraester:



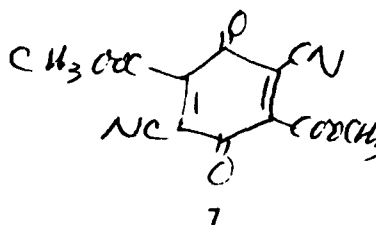
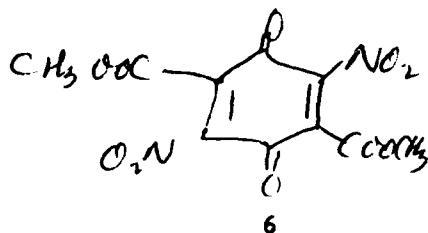
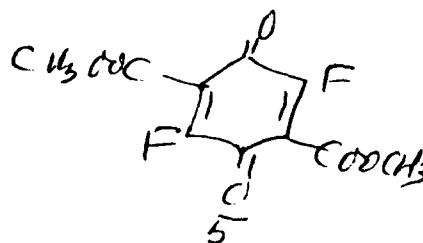
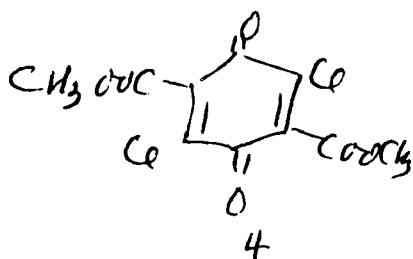
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Coupling attempts using the dibromo derivative of acetonedicarboxylic ester also failed.

Next, Claisen self-condensation of tetraethyl 1,1,2,2-ethane-tetracarboxylate was found to give very low yields of the tetrahydro derivative corresponding to 3.

In the final phase of our work, the readily available 4 was converted to three derivatives 5-7 by reaction with alkali or thallium salts:

These were considered as possible intermediates for new thermally stable polymers.



Yields were low, probably because of the unusual chemistry of these electrophilic quinones, as known for tetracyano-p-benzoquinone (4) and also because the aqueous work-up of the synthesis led to the dihydroxy quinone dicarboxylate (5).

This area does not seem promising for practical syntheses of thermally stable polymers.

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